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(54) Preparation of low density, low modulus ethylene copolymers in a fluidized bed.

(57) Ethylene copolymers having a density of less than 0.91 g/cm<sup>3</sup> and a 1% secant modulus of less than 140,000 kPa are continuously prepared in a fluidized bed without particle agglomeration by continuously contacting, in such fluidized bed, at a temperature of from 10°C up to 80°C, a gaseous mixture containing (a) ethylene and at least one higher alpha olefin in a molar ratio of such higher alpha olefin to ethylene of from 0.35:1 to 8.0:1, and (b) at least 25 mol percent of a diluent gas, with a catalyst composition prepared by forming a precursor composition from a magnesium compound, titanium compound, and electron donor compound; diluting said precursor composition with an inert carrier; and activating the diluted precursor composition with an organoaluminum compound.

PREPARATION OF LOW DENSITY, LOW MODULUS  
ETHYLENE COPOLYMERS IN A FLUIDIZED BED

5 This invention relates to a process for  
preparing very low density, low modulus ethylene  
copolymers in a fluidized bed. More particularly,  
this invention relates to a fluid bed process for  
preparing ethylene copolymers having a density of  
less than  $0.91 \text{ g/cm}^3$  and a  $1\frac{1}{2}$  secant modulus of  
10 less than 140,000 kPa.

Ethylene copolymers having a density of  
from  $0.91 \text{ g/cm}^3$  to  $0.96 \text{ g/cm}^3$  can be prepared in  
a fluidized bed as described in U.S. patents  
15 4,302,565 and 4,302,566 by continuously  
copolymerizing ethylene with one or more higher  
alpha olefin monomers by means of a catalyst  
composition prepared by (1) forming a precursor  
composition from a magnesium compound, titanium  
20 compound and electron donor compound, (2) diluting  
said precursor composition with an inert carrier  
material, and (3) activating the precursor  
composition with an organoaluminum compound. The  
copolymers prepared in accordance with these patents  
25 are relatively high modulus, stiff materials which  
are generally useful in the preparation of films and  
injection molded articles. However, these patents  
do not describe how low modulus copolymers having a  
density of less than  $0.91 \text{ g/cm}^3$  can be prepared.  
30 Such low modulus copolymers would be useful in the  
preparation of tubing and hoses, and in other

applications where flexibility and toughness are desirable.

When attempts have been made to produce low modulus ethylene copolymers having a density of less than  $0.91 \text{ g/cm}^3$  by modifying the procedure of the  
5       aforementioned U.S. patents, e.g., by increasing the concentration of higher alpha olefin comonomers in the reactor, it has been found that tacky, gummy polymer particles are produced. Because of their  
10       sticky character, such particles have a tendency to cohere to each other and form large agglomerates. After a short time these agglomerates reach a size too big to sustain fluidization in the reactor bed. As a result, polymerization comes to a halt after  
15       the production of only a small amount of the desired copolymer because of the reactor fouling caused by these large agglomerates.

U.K. patent specifications 2 033 910 A, 2 034 336 A, 2 034 723 A and 2 066 274 A disclose  
20       the preparation of ethylene copolymers and terpolymers by the polymerization of monomeric olefin mixtures in vapor phase in the presence of a catalyst composition including (1) an organoaluminum compound and (2) a solid substance containing a  
25       magnesium-containing compound and a titanium compound and/or a vanadium compound. However, these references do not report the conditions required to avoid the reactor fouling caused by particle agglomeration when attempting to produce polymers  
30       having a density of less than  $0.91 \text{ g/cm}^3$  in a fluidized bed so as to enable polymerization to proceed on a continuous basis at high polymer

productivity. Furthermore, these references do not illustrate how polymerization can be effected without lengthy ball milling of the catalyst employed.

5 U.K. patent specifications 2 006 232 A,  
2 053 246 A and 2 053 935 A disclose the preparation  
of ethylene copolymers and terpolymers by the  
polymerization of monomeric olefin mixtures in a  
fluidized bed in the presence of a catalyst  
10 composition including (1) an organometallic  
component and (2) a titanium-containing component.  
However, these references likewise do not report the  
conditions required to avoid particle agglomeration  
and sustain polymerization on a continuous basis at  
high polymer productivity when attempting to produce  
polymers having a density of less than 0.91  
g/cm<sup>3</sup>. Furthermore, these references do not  
illustrate how polymerization can be effected  
without initially preparing a prepolymer.

20

In accordance with the present invention it  
has now been discovered that ethylene copolymers  
having a density below 0.91 g/cm<sup>3</sup> and a 1% secant  
modulus below 140,000 kPa can be continuously  
25 prepared by means of a fluidized bed polymerization  
process by continuously contacting, in such  
fluidized bed, at a temperature of from 10°C up to  
80°C, a gaseous mixture containing (a) ethylene and  
at least one higher alpha olefin in a molar ratio of  
30 such higher alpha olefin to ethylene of from 0.35:1  
to 8.0:1, and (b) at least 25 mol percent of a  
diluent gas, with a catalyst composition prepared by

forming a precursor composition from a magnesium compound, titanium compound, and electron donor compound; diluting said precursor composition with an inert carrier; and activating the diluted precursor composition with an organoaluminum compound.

Figure 1 is a graph of the 1% secant modulus of low modulus ethylene copolymers vs. reaction temperatures employed to copolymerize ethylene with higher alpha olefins, such as propylene or butene, by means of a fluid bed process employing the catalyst compositions of the present invention. The graph illustrates the operable polymerization temperatures which may be employed to produce ethylene copolymers of a given secant modulus without polymer agglomeration employing a gaseous mixture containing 50 mol percent of diluent gas and a reactor pressure of 2000 kPa. The region above the line is operable, while that below the line is inoperable.

Fluid bed reactors suitable for continuously preparing ethylene copolymers have been previously described and are well known in the art. Fluid bed reactors useful for this purpose are described, e.g., in U.S. patents 4,302,565 and 4,302,566, the disclosures of which are incorporated herein by reference. Said patents likewise disclose catalyst compositions suitable for preparing such copolymers.

In order to produce ethylene copolymers having a density below  $0.91 \text{ g/cm}^3$  by means of a fluid bed process, it is necessary to employ gaseous reaction mixtures containing higher amounts of higher alpha olefin comonomer vis-a-vis the amount of ethylene employed than are employed to produce copolymers having a density greater than  $0.91 \text{ g/cm}^3$ . By the addition of progressively larger amounts of such higher olefin to the mixture, copolymers having progressively lower densities are obtained at any given melt index. The amount of higher olefin needed to achieve copolymers of a given density will vary from olefin to olefin, under the same conditions, with larger amounts of such higher olefin required as the number of carbon atoms in the olefin decreases. Generally, in order to produce copolymers having a density of less than  $0.91 \text{ g/cm}^3$ , it is necessary to employ reaction mixtures containing such higher olefin and ethylene in a molar ratio of higher olefin to ethylene of at least 0.35:1. Usually, mixtures containing such higher olefin and ethylene in a molar ratio of from 0.35:1 to 8.0:1 are employed for this purpose, with molar ratios of from 0.6:1 to 7.0:1 being preferred.

The higher alpha olefins which can be polymerized with ethylene to produce the low density, low modulus copolymers of the present invention can contain from 3 to 8 carbon atoms. These alpha olefins should not contain any branching on any of their carbon atoms closer than two carbon atoms removed from the double bond. Suitable alpha olefins include propylene, butene-1, pentene-1,

hexene-1, 4-methylpentene-1, heptene-1 and octene-1. The preferred alpha olefins are propylene, butene-1, hexene-1, 4-methylpentene-1 and octene-1.

5           If desired, one or more dienes, either conjugated or non-conjugated, may be present in the reaction mixture. Such dienes may be employed in an amount of from 0.1 mol percent to 10 mol percent of the total gaseous mixture fed to the fluid bed,  
10           preferably in an amount of from 0.1 mol percent to 8 mol percent. Such dienes may include, for example, butadiene, 1,4-hexadiene, 1,5-hexadiene, vinyl norbornene, ethylidene norbornene and dicyclopentadiene.

15           In order to prevent the formation of polymer agglomerates and sustain polymerization on a continuous basis when employing reaction mixtures containing the high ratios of higher alpha olefin comonomer to ethylene required to produce the  
20           desired copolymers having a density below 0.91 g/cm<sup>3</sup>, it has been found necessary to dilute the reaction mixture with a large quantity of a diluent gas. Dilution of the reaction mixture with a  
25           diluent gas in this manner serves to reduce the tackiness of the polymers produced which is the main cause of such agglomeration. Ordinarily the diluent gas should make up at least 25 mol percent of the total gaseous mixture fed to the fluid bed in order  
30           to prevent such agglomeration. Preferably, the gaseous mixture contains from 33 mol percent to 95 mol percent of such gas, most preferably from 40 mol percent to 70 mol percent. By a "diluent" gas is

meant a gas which is nonreactive under the conditions employed in the polymerization reactor, i.e., does not decompose and/or react with the polymerizable monomers and the components of the catalyst composition under the polymerization conditions employed in the reactor other than to terminate polymer chain growth. In addition, such gas should be insoluble in the polymer product produced so as not to contribute to polymer tackiness. Among such gases are nitrogen, argon, helium, methane, ethane, and the like.

Hydrogen may also be employed as a diluent gas. In this event, the diluent serves not only to dilute the reaction mixture and prevent polymer agglomeration, but also acts as a chain transfer agent to regulate the melt index of the copolymers produced by the process. Generally, the reaction mixture contains hydrogen in an amount sufficient to produce a hydrogen to ethylene mol ratio of from 0.01:1 to 0.5:1. In addition to hydrogen, other chain transfer agents may be employed to regulate the melt index of the copolymers.

The gaseous reaction mixture should, of course, be substantially free of catalyst poisons, such as moisture, oxygen, carbon monoxide, carbon dioxide, acetylene and the like.

In addition to diluting the reaction mixture with a diluent gas, it has also been found necessary to maintain a relatively low temperature in the reactor in order to prevent polymer agglomeration and sustain polymerization on a continuous basis. The temperature which can be



employed varies directly with the concentration of diluent gas present in such mixture, with higher concentrations of diluent gas permitting the use of somewhat higher temperatures without adverse effects. Likewise, the lower the concentration of the higher alpha olefin comonomer in the reaction mixture vis-a-vis the ethylene concentration, i.e., the higher the density and modulus of the copolymer being produced, the higher the temperature which can be employed. Generally, however, in order to continuously produce copolymers having a density below  $0.91 \text{ g/cm}^3$  and a 1% secant modulus below 140,000 kPa while at the same time preventing polymer agglomeration, the temperature should not be permitted to rise above  $80^\circ\text{C}$ . On the other hand, the temperature employed must be sufficiently elevated to prevent substantial condensation of the reaction mixture, including diluent gas, to the liquid state, as such condensation will cause the polymer particles being produced to cohere to each other and likewise aggravate the polymer agglomeration problem. This difficulty is normally associated with the use of alpha olefins having 5 or more carbon atoms which have relatively high dew points. While some minor condensation is tolerable, anything beyond this will cause reaction fouling. Usually temperatures of from  $10^\circ\text{C}$  to  $60^\circ\text{C}$  are employed to produce copolymers having a density of from  $0.86 \text{ g/cm}^3$  to  $0.90 \text{ g/cm}^3$  and a secant modulus of from 600 kPa to 100,000 kPa. More elevated temperatures of from  $60^\circ\text{C}$  up to  $80^\circ\text{C}$  are ordinarily employed in the production of copolymers

having a density of from  $0.90 \text{ g/cm}^3$  up to  $0.91 \text{ g/cm}^3$  and a secant modulus of from 100,000 kPa up to 140,000 kPa. Figure 1 illustrates the maximum polymerization temperatures which may be employed to produce ethylene copolymers of a given secant modulus without polymer agglomeration when the reaction mixture is diluted with 50 mol percent of a diluent gas. The region above the line is operable, while that below the line is inoperable.

Pressures of up to about 7000 kPa can be employed in the process, although pressures of from about 70 kPa to 2500 kPa are preferred.

In order to maintain a viable fluidized bed, the superficial gas velocity of the gaseous reaction mixture through the bed must exceed the minimum flow required for fluidization, and preferably is at least 0.2 feet per second above the minimum flow. Ordinarily the superficial gas velocity does not exceed 5.0 feet per second, and most usually no more than 2.5 feet per second is sufficient.

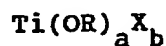
The catalyst compositions employed in the process of the present invention are produced by forming a precursor composition from a magnesium compound, titanium compound, and electron donor compound; diluting said precursor composition with an inert carrier; and activating the diluted precursor composition with an organoaluminum compound.

The precursor composition is formed by dissolving at least one titanium compound and at least one magnesium compound in at least one

electron donor compound at a temperature of from about 20°C up to the boiling point of the electron donor compound. The titanium compound(s) can be added to the electron donor compound(s) before or  
5 after the addition of the magnesium compound(s), or concurrent therewith. The dissolution of the titanium compound(s) and the magnesium compound(s) can be facilitated by stirring, and in some instances by refluxing, these two compounds in the  
10 electron donor compound(s). After the titanium compound(s) and the magnesium compound(s) are dissolved, the precursor composition may be isolated by crystallization or by precipitation with an aliphatic or aromatic hydrocarbon containing from 5  
15 to 8 carbon atoms, such as hexane, isopentane or benzene. The crystallized or precipitated precursor composition may be isolated in the form of fine, free-flowing particles having an average particle size of from about 10 microns to about 100 microns  
20 after drying at temperatures up to 60°C.

About 0.5 mol to about 56 mols, and preferably about 1 mol to about 10 mols, of the magnesium compound(s) are used per mol of the titanium compound(s) in preparing the precursor  
25 composition.

The titanium compound(s) employed in preparing the precursor composition has the structure



30 wherein R is an aliphatic or aromatic hydrocarbon radical containing from 1 to 14 carbons atoms, or COR' where R' is an aliphatic or aromatic

hydrocarbon radical containing from 1 to 14 carbon atoms.

X is selected from the group consisting of Cl, Br, I, and mixtures thereof,

5 a is 0, 1 or 2, b is 1 to 4 inclusive, and  
a + b = 3 or 4.

Suitable titanium compounds include  
 $\text{TiCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{Ti}(\text{OCH}_3)\text{Cl}_3$ ,  $\text{Ti}(\text{OC}_6\text{H}_5)\text{Cl}_3$ ,  
10  $\text{Ti}(\text{OCOCH}_3)\text{Cl}_3$  and  $\text{Ti}(\text{OCOC}_6\text{H}_5)\text{Cl}_3$ .  $\text{TiCl}_3$  is

preferred because catalysts containing this material  
show higher activity at the low temperatures and  
monomer concentrations employed in the process of  
the present invention.

15 The magnesium compound(s) employed in  
preparing the precursor composition has the structure



wherein X is selected from the group  
consisting of Cl, Br, I, and mixtures thereof.

Suitable magnesium compounds include  
20  $\text{MgCl}_2$ ,  $\text{MgBr}_2$  and  $\text{MgI}_2$ . Anhydrous  $\text{MgCl}_2$  is  
particularly preferred.

The electron donor compound(s) employed in  
preparing the precursor composition is an organic  
compound which is liquid at 25°C and in which the  
25 titanium and magnesium compounds are soluble. The  
electron donor compounds are known as such, or as  
Lewis bases.

Suitable electron donor compounds include  
the alkyl esters of aliphatic and aromatic  
30 carboxylic acids, aliphatic ethers, cyclic ethers  
and aliphatic ketones. Among these electron donor  
compounds the preferable ones are alkyl esters of

saturated aliphatic carboxylic acids containing from 1 to 4 carbon atoms; alkyl esters of aromatic carboxylic acids containing from 7 to 8 carbon atoms; aliphatic ethers containing from 2 to 8 carbon atoms, preferably from 4 to 5 carbon atoms; cyclic ethers containing from 4 to 5 carbon atoms, preferably mono- or di-ethers containing 4 carbon atoms; and aliphatic ketones containing from 3 to 6 carbon atoms, preferably from 3 to 4 carbon atoms.

The most preferred of these electron donor compounds include methyl formate, ethyl acetate, butyl acetate, ethyl ether, tetrahydrofuran, dioxane, acetone and methyl ethyl ketone.

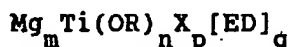
After the precursor composition has been prepared it is diluted with an inert carrier material by (1) mechanically mixing or (2) impregnating such composition into the carrier material.

Mechanical mixing of the inert carrier and precursor composition is effected by blending these materials together using conventional techniques. The blended mixture suitably contains from about 3 percent by weight to about 50 percent by weight of the precursor composition.

Impregnation of the inert carrier material with the precursor composition may be accomplished by dissolving the precursor composition in the electron donor compound, and then admixing the support with the dissolved precursor composition to impregnate the support. The solvent is then removed by drying at temperatures up to about 85°C.

The support may also be impregnated with the precursor composition by adding the support to a solution of the chemical raw materials used to form the precursor composition in the electron donor compound, without isolating the precursor composition from said solution. The excess electron donor compound is then removed by drying at temperatures up to about 85°C.

When thus made as disclosed above the blended or impregnated precursor composition has the formula



wherein R is an aliphatic or aromatic hydrocarbon radical containing from 1 to 14 carbon atoms, or COR' wherein R' is also an aliphatic or aromatic hydrocarbon radical containing from 1 to 14 carbon atoms,

X is selected from the group consisting of Cl, Br, I, and mixtures thereof,

ED is an electron donor compound,

m is 0.5 to 56, preferably 1.5 to 5,

n is 0, 1 or 2,

p is 2 to 116, preferably 6 to 14, and

q is 2 to 85, preferably 3 to 10.

Suitably, the impregnated carrier material contains from about 3 percent by weight to about 50 percent by weight, preferably from about 10 percent by weight to about 30 percent by weight, of the precursor composition.

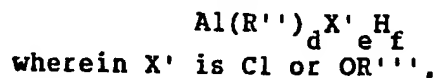
The carrier materials employed to dilute the precursor composition are solid, particulate, porous materials which are inert to the other

components of the catalyst composition, and to the other active components of the reaction system. These carrier materials include inorganic materials such as oxides of silicon and/or aluminum. The carrier materials are used in the form of dry powders having an average particle size of from about 10 microns to about 250 microns, preferably from about 20 microns to about 150 microns. These materials are also porous and have a surface area of at least 3 square meters per gram, and preferably at least 50 square meters per gram. Catalyst activity or productivity can apparently be improved by employing a silica support having average pore sizes of at least 80 Angstrom units, preferably at least 100 Angstrom units. The carrier material should be dry, that is, free of absorbed water. Drying of the carrier material can be effected by heating, e.g., at a temperature of at least 600°C when silica is employed as the support. Alternatively, when silica is employed, it may be dried at a temperature of at least 200°C and treated with about 1 weight percent to about 8 weight percent of one or more of the aluminum activator compounds described below. Modification of the support with an aluminum compound in this manner provides the catalyst composition with increased activity and also improves polymer particle morphology of the resulting ethylene copolymers. Other organometallic compounds, such as diethylzinc, may also be used to modify the support.

To be useful in producing ethylene copolymers, the precursor composition must be

- 15 -

activated with a compound capable of transforming the titanium atoms in the precursor composition to a state which will cause ethylene to effectively copolymerize with higher alpha olefins. Such  
 5 activation is effected by means of an organoaluminum compound having the structure



R'' and R''' are saturated hydrocarbon  
 10 radicals containing from 1 to 14 carbon atoms, which radicals may be the same or different,

e is 0 to 1.5,

f is 0 or 1, and

d + e + f = 3.

15 Such activator compounds can be employed individually or in combination thereof and include compounds such as  $\text{Al}(\text{C}_2\text{H}_5)_3$ ,  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ ,  
 $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3$ ,  $\text{Al}(\text{C}_2\text{H}_5)_2\text{H}$ ,  $\text{Al}(\text{C}_2\text{H}_5)_2(\text{OC}_2\text{H}_5)$ ,  
 $\text{Al}(\text{i-C}_4\text{H}_9)_3$ ,  $\text{Al}(\text{i-C}_4\text{H}_9)_2\text{H}$ ,  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  
 20  $\text{Al}(\text{C}_8\text{H}_{17})_3$ .

If desired, the precursor composition may be partially activated before it is introduced into the polymerization reactor. However, any activation undertaken outside of the polymerization reactor  
 25 should be limited to the addition of an amount of activator compound which does not raise the molar ratio of activator compound:electron donor in the precursor composition beyond 1.4:1. Preferably, when activation is effected outside the reactor in  
 30 this manner, the activator compound is employed in an amount which will provide the precursor



composition with an activator compound:electron donor molar ratio of from about 0.1:1 to about 1.0:1. Such partial activation is carried out in a hydrocarbon solvent slurry followed by drying of the resulting mixture, to remove the solvent, at temperatures of from about 20°C to about 80°C., preferably from about 50°C to about 70°C. The resulting product is a free-flowing solid particulate material which can be readily fed to the polymerization reactor where the activation is completed with additional activator compound which can be the same or a different compound.

Alternatively, when an impregnated precursor composition is employed, it may, if desired, be completely activated in the polymerization reactor without any prior activation outside of the reactor, in the manner described in European patent publication No. 12,148.

The partially activated or totally unactivated precursor composition and the required amount of activator compound necessary to complete activation of the precursor composition are preferably fed to the reactor through separate feed lines. The activator compound may be sprayed into the reactor in the form of a solution thereof in a hydrocarbon solvent such as isopentane, hexane, or mineral oil. This solution usually contains from about 2 weight percent to about 30 weight percent of the activator compound. The activator compound is added to the reactor in such amounts as to provide, in the reactor, a total aluminum:titanium molar

ratio of from about 10:1 to about 400:1, preferably from about 25:1 to about 60:1.

5 In the continuous gas phase fluid bed process disclosed herein, discrete portions of the partially activated or totally unactivated precursor composition are continuously fed to the reactor, with discrete portions of the activator compound needed to complete the activation of the partially activated or totally unactivated precursor  
10 composition, during the continuing polymerization process in order to replace active catalyst sites that are expended during the course of the reaction.

By operating under the polymerization conditions described herein it is possible to  
15 continuously polymerize ethylene in a fluidized bed with one or more higher alpha olefins containing from 3 to 8 carbon atoms, and optionally also with one or more dienes, to produce ethylene polymers having a density below  $0.91 \text{ g/cm}^3$  and a 1% secant modulus below 140,000 kPa. By "continuously  
20 polymerize" as used herein is meant the capability of uninterrupted polymerization for weeks at a time, i.e., at least in excess of 168 hours, and usually in excess of 1000 hours without reactor fouling due to the production of large agglomerations of polymer.  
25

The copolymers produced in accordance with the process of the present invention usually have a density of from  $0.86 \text{ g/cm}^3$  to  $0.90 \text{ g/cm}^3$  and a 1% secant modulus of from 600 kPa to 100,000 kPa.  
30 Such copolymers contain no more than 94 mol percent of polymerized ethylene and at least 6 mol percent of polymerized alpha olefin containing from 3 to 8

carbon atoms and, optionally, polymerized diene. When polymerized diene is present, the polymer contains from 0.01 mol percent to 10 mol percent of at least one such diene, from 6 mol percent to 55 mol percent of at least one polymerized alpha olefin containing from 3 to 8 carbon atoms, and from 35 mol percent to 94 mol percent of polymerized ethylene.

The molar ratios of propylene to ethylene which must be employed in the reaction mixture to produce copolymers having a given propylene content are illustrated in Table 1 below. When alpha olefins higher than propylene are employed, like results can be obtained with lower ratios of such higher alpha olefin to ethylene in the reaction mixture.

TABLE 1

$C_3H_6/C_2H_4$ Ratio In Reaction Mixture	Mol % $C_3H_6$ In Copolymer	Mol % $C_2H_4$ In Copolymer
0.7	6	94
1.5	12	88
3.0	25	75
6.0	50	50
8.0	62	38

The ethylene polymers produced in accordance with the process of the present invention have a standard or normal load melt index of from greater than 0 g/10 minutes to about 25.0 g/10 minutes, preferably of from about 0.2 g/10 minutes to about 4.0 g/10 minutes. Such polymers have a high load melt index (HLMI) of from greater than 0 g/10 minutes to about 1000 g/10 minutes. The melt index of a polymer varies inversely with its molecular weight and is a function of the

polymerization temperature of the reaction, the density of the polymer, and the hydrogen/monomer ratio in the reaction system. Thus, the melt index is raised by increasing the polymerization  
5 temperature, by increasing the ratio of higher alpha olefin to ethylene in the reaction system, and/or by increasing the hydrogen/monomer ratio.

The ethylene polymers produced in accordance with the process of the present invention  
10 have a melt flow ratio (MFR) of from about 22 to about 40, preferably of from about 26 to about 35. Melt flow ratio is another means of indicating the molecular weight distribution ( $M_w/M_n$ ) of a polymer. An MFR in the range of from about 22 to  
15 about 40 corresponds to a  $M_w/M_n$  of from about 2.7 to about 6.5, and an MFR in the range of from about 26 to about 35 corresponds to a  $M_w/M_n$  of from about 2.9 to about 4.8.

The ethylene polymers produced in accordance with the process of the present invention  
20 have a residual catalyst content, in terms of parts per million of titanium metal, or less than 10 parts per million (ppm) at a productivity level of at least 100,000 pounds of polymer per pound of  
25 titanium. The copolymers are readily produced with such catalyst compositions at productivities of up to about 500,000 pounds of polymer per pound of titanium.

The ethylene polymers produced in accordance with the process of the present invention  
30 are granular materials having an average particle size of the order of from about 0.01 to about 0.07

inches, usually of from about 0.02 to about 0.05 inches, in diameter. The particle size is important for the purpose of readily fluidizing the polymer particles in the fluid bed reactor. These granular materials also contain no more than 4.0 percent of fine particles having a diameter of less than 0.005 inches.

The ethylene polymers produced in accordance with the process of the present invention have a bulk density of from about 16 pounds per cubic foot to about 31 pounds per cubic foot.

The following Examples are designed to illustrate the process of the present invention and are not intended as a limitation upon the scope thereof.

The properties of the polymers produced in the Examples was determined by the following test methods:

#### Density

ASTM D-1505. A plaque is made and conditioned for one hour at 100°C to approach equilibrium crystallinity. Measurement for density is then made in a density gradient column and density values are reported as grams/cm<sup>3</sup>.

#### Melt Index (MI)

ASTM D-1238, Condition E. Measured at 190°C and reported as grams per 10 minutes.

#### Flow Index (HLMI)

ASTM D-1238, Condition F. Measured at 10 times the weight used in the melt index test above.

Melt Flow Ratio (MFR)

Ratio of Flow Index : Melt Index

Productivity

5 A sample of the resin product is ashed, and  
the weight percent of ash is determined. Since the  
ash is essentially composed of the catalyst, the  
productivity is thus the pounds of polymer produced  
per pound of total catalyst consumed. The amount of  
10 Ti, Mg and halide in the ash are determined by  
elemental analysis.

Bulk Density

ASTM D-1895, Method B. The resin is poured  
via 3/8" diameter funnel into a 400 ml graduated  
cylinder to the 400 ml line without shaking the  
15 cylinder, and weighed by difference.

Average Particle Size

Calculated from sieve analysis data  
measured according to ASTM D-1921, Method A, using a  
500 g sample. Calculations are based on weight  
20 fractions retained on the screens.

n-Hexane Extractables

(FDA test used for polyethylene film  
intended for food contact applications). A 200  
square inch sample of 1.5 mil gauge film is cut into  
25 strips measuring 1" x 6" and weighed to the nearest  
0.1 mg. The strips are placed in a vessel and  
extracted with 300 ml. of n-hexane at  $50 \pm 1^\circ\text{C}$  for 2  
hours. The extract is then decanted into tared  
culture dishes. After drying the extract in a  
30 vacuum desiccator the culture dish is weighed to the

nearest 0.1 mg. The extractables, normalized with respect to the original sample weight, is then reported as the weight fraction of n-hexane extractables.

5 Molecular Weight Distribution,  $M_w/M_n$

Gel Permeation Chromatography. Styrogel column packing: (Pore size packing sequence is  $10^7$ ,  $10^5$ ,  $10^4$ ,  $10^3$ , 60A°). Solvent is perchloroethylene at 117°C. Detection: infrared at 3.45 $\mu$ .

Melting Point, °C

Melting point was determined on a 5-6 mil thick film sample using a duPont differential thermal analyzer, Model 990. The sample was rapidly heated under nitrogen to 150°C, held isothermally at this temperature for 5 minutes, cooled at a rate of 10°C/minute to 50°C, and then re-heated at a rate of 10°C/minute until the softening point was reached.

% Crystallinity

Crystallinity was determined by x-ray diffraction using a Norelco XRG-500 X-ray diffractometer with copper  $K_\alpha$  radiation. Crystallinity was calculated from the integrated intensity of the (020) reflection.

25 1% Secant Modulus

ASTM D-638. Film strips 10" x 0.5" are clamped at a 5 inch gauge length and deformed at a jaw separation rate of 0.2 in./min. A force elongation trace is determined. Secant modulus is

the slope of a line drawn from the origin to the load at 1% deformation. Deformation is determined by crosshead position. Normalizing by the specimen's undeformed cross-sectional area, secant modulus is reported in kPa.

#### Tensile Strength and Elongation

ASTM D-638. Film strips 1" x 5" are clamped at a 2 inch gauge length and deformed at a jaw separation rate of 20 in./min. Tensile strength is the engineering stress developed at break. Elongation at break is measured by following the deformation of 1" gauge marks placed on the film sample and is reported in percent.

#### Example 1

##### Impregnation of Support with Precursor

(a) In a 12 liter flask equipped with a mechanical stirrer were placed 41.8g (0.439 mol) of anhydrous  $\text{MgCl}_2$  and 2.5 liters of tetrahydrofuran (THF). To this mixture, 27.7g (0.146 mol) of  $\text{TiCl}_4$  were added dropwise over a 1/2 hour period. The mixture was then heated at 60°C. for another 1/2 hour in order to completely dissolve the material.

Five hundred grams (500 g) of silica was dehydrated by heating at a temperature of 600°C and slurried in 3 liters of isopentane. The slurry was stirred while 186 ml. of a 20 percent by weight solution of triethylaluminum in hexane was added thereto over a 1/4 hour period. The resulting mixture was then dried under a nitrogen purge at 60°C over a period of about 4 hours to provide a



- 24 -

dry, free-flowing powder containing 5.5 percent by weight of the aluminum alkyl.

5 The treated silica was then added to the solution prepared as above. The resulting slurry was stirred for 1/4 hour and then dried under a nitrogen purge at 60°C over a period of about 4 hours to provide a dry, impregnated, free-flowing powder.

10 (b) The procedure was repeated employing 29.0g (0.146 mol) of  $\text{TiCl}_3 \cdot 0.33 \text{ AlCl}_3$  in place of  $\text{TiCl}_4$ .

#### Example 2

##### Preparation of Partially Activated Precursor

15 (a) The silica-impregnated precursor composition prepared in accordance with Example 1(a) was slurried in 3 liters of anhydrous isopentane and stirred while a 20 percent by weight solution of diethylaluminum chloride in anhydrous hexane was added thereto over a 1/4 hour period. The  
20 diethylaluminum chloride solution was employed in an amount sufficient to provide 0.4 mols of this compound per mol of tetrahydrofuran in the precursor. After addition of the diethylaluminum chloride was completed, stirring was continued for  
25 an additional 1/4 to 1/2 hour while a 20 percent by weight solution of tri-n-hexylaluminum in anhydrous hexane was added in an amount sufficient to provide 0.6 mols of this compound per mol of tetrahydrofuran in the precursor. The mixture was then dried under  
30 a nitrogen purge at a temperature of 65±10°C over a period of about 4 hours to provide a dry, free-

flowing powder. This material was stored under dry nitrogen until it was needed.

(b) The silica-impregnated precursor composition prepared in accordance with Example 1(b) was partially activated with diethylaluminum chloride and tri-n-hexylaluminum employing the same procedure as in 2(a) except that the tri-n-hexylaluminum was employed in an amount sufficient to provide 0.4 mols of this compound per mol of tetrahydrofuran in the precursor.

(c) The silica-impregnated precursor composition prepared in accordance with Example 1(b) was partially activated with diethylaluminum chloride and tri-n-hexylaluminum employing the same procedure as in 2(a) except that each compound was employed in an amount sufficient to provide 0.3 mols of such compound per mol of tetrahydrofuran in the precursor.

#### Examples 3-4

Ethylene was copolymerized with butene-1 under varying reaction conditions in a fluid bed reactor system similar to the one described and illustrated in U.S. patents 4,302,565 and 4,302,566. The polymerization reactor had a lower section 10 feet high and 13-1/2 inches in diameter, and an upper section 16 feet high and 23-1/2 inches in diameter.

In each polymerization, silica-impregnated precursor composition prepared in accordance with Example 1(a) and partially activated in accordance with Example 2(a) was fed to the polymerization reactor along with a 5 percent solution of triethyl-

aluminum in isopentane so as to provide a completely activated catalyst in the reactor having an aluminum:titanium molar ratio of from 15:1 to 55:1.

- 5 Table 2 below summarizes the reaction conditions employed in each polymerization, the properties of the polymers produced by such polymerizations, and the productivity of the catalyst system employed in terms of residual titanium in the copolymer.

TABLE 2

Example		3	4
<u>Polymerization Conditions</u>			
	Temperature, °C	55	55
5	Pressure, kPa	2068	2068
	Gas Velocity, ft./sec.	2.2	2.2
	Space-Time Yield (lbs/hr/ft <sup>3</sup> )	5.3	4.5
	Butene/Ethylene Mol Ratio	0.75	0.91
10	Hydrogen/Ethylene Mol Ratio	0.25	0.21
	Mol % N <sub>2</sub> in Reaction Mixture	41	52
	Mol % H <sub>2</sub> in Reaction Mixture	6.4	4.7
	Molar Ratio Al:Ti in Completely Activated Catalyst	50	46
15	<u>Polymer Properties</u>		
	Density, g/cm <sup>3</sup>	0.900	0.898
	Melt Index, g/10 Min.	1.2	1.2
	Flow Index, g/10 Min.	33.3	36.7
	Melt Flow Ratio	27.5	30.8
20	Bulk Density, lbs/ft <sup>3</sup>	20.5	18.8
	Average Particle Size, in.	0.03	0.03
	n-Hexane Extractables, %	9.8	14.3
	Mol. Wt. Distribution, $M_w/M_n$	4.8	4.4
	Melting Point, °C	120.8	117.4
25	% Crystallinity	32.4	19.0
	1% Secant Modulus, kPa	90,738	69,047
	Tensile Strength, kPa	19,906	16,720
	Elongation, %	1,009	918
	<u>Productivity</u>		
30	ppm Ti in Copolymer	4.6	6.1

It is noted that when the reaction temperature in Example 4 was increased to 65°C, reactor fouling occurred due to particle agglomeration forcing a halt to polymerization.

5

Examples 5-6

Ethylene was copolymerized with propylene under varying reaction conditions employing the same fluid bed reactor system and catalyst system employed in examples 3-4.

10

Table 3 below summarizes the reaction conditions employed in each polymerization, and the properties of the polymers produced by such polymerizations.

Table 3

<u>Example</u>		<u>5</u>	<u>6</u>
<u>Polymerization Conditions</u>			
	Temperature, °C	58	57
5	Pressure, kPa	2068	2068
	Gas Velocity, ft./sec.	1.9	1.9
	Space-Time Yield (lbs./hr./ft <sup>3</sup> )	4.4	2.8
	Propylene/Ethylene Mol Ratio	1.0	1.5
10	Hydrogen/Ethylene Mol Ratio	0.18	0.24
	Mol % N <sub>2</sub> in Reaction Mixture	39	46
	Mol % H <sub>2</sub> in Reaction Mixture	5.1	4.8
	Molar Ratio Al:Ti in Completely Activated Catalyst	-	17
15	<u>Polymer Properties</u>		
	Density, g/cm <sup>3</sup>	0.899	0.898
	Melt Index, g/10 Min.	1.1	1.1
	Flow Index, g/10 Min.	39.0	-
	Melt Flow Ratio	31.4	-
20	Bulk Density, lbs/ft <sup>3</sup>	21.8	18.2
	Average Particle Size, in.	0.02	0.03
	n-Hexane Extractables, %	9.3	15.1
	Mol. Wt. Distribution, M <sub>w</sub> /M <sub>n</sub>	4.3	4.2
	Melting Point, °C	114.8	104.4
25	% Crystallinity	16.0	18.3
	1% Secant Modulus, kPa	99,591	57,217
	Tensile Strength, kPa	13,225	9,653
	Elongation, %	927	973

It is noted that when operating at substantially the same conditions as in Example 6, but employing a reaction mixture containing 36 mol percent nitrogen and a reaction temperature of 65°C, reactor fouling occurred due to particle agglomeration forcing a halt to polymerization.

#### Examples 7-8

Ethylene was copolymerized with propylene under varying reaction conditions employing the same fluid bed reactor system employed in examples 3-4.

In each polymerization, silica-impregnated precursor composition prepared in accordance with Example 1(b) and partially activated in accordance with Example 2(b) was fed to the polymerization reactor along with a 5 percent solution of triethylaluminum in isopentane so as to provide a completely activated catalyst in the reactor having an aluminum:titanium molar ratio of from 40:1 to 55:1.

Table 4 below summarizes the reaction conditions employed in each polymerization, the properties of the polymers produced by such polymerizations, and the productivity of the catalyst system employed in terms of residual titanium in the copolymer.

		<u>Table 4</u>	
<u>Example</u>		<u>7</u>	<u>8</u>
<u>Polymerization Conditions</u>			
	Temperature, °C	55	35
5	Pressure, kPa	2068	2068
	Gas Velocity, ft./sec.	2.3	2.3
	Space-Time Yield (lbs./hr./ft <sup>3</sup> )	4.5	4.8
	Propylene/Ethylene Mol Ratio	1.1	1.0
10	Hydrogen/Ethylene Mol Ratio	0.14	0.21
	Mol % N <sub>2</sub> in Reaction Mixture	52.5	63
	Mol % H <sub>2</sub> in Reaction Mixture	3.0	3.5
	Molar Ratio Al:Ti in Completely Activated Catalyst	50	51
15	<u>Polymer Properties</u>		
	Density, g/cm <sup>3</sup>	0.895	0.885
	Melt Index, g/10 Min.	1.6	0.9
	Flow Index, g/10 Min.	52.6	32.9
	Melt Flow Ratio	32.9	36.6
20	Bulk Density, lbs/ft <sup>3</sup>	17.8	24.2
	Average Particle Size, in.	0.06	0.04
	n- Hexane Extractables, %	23.2	28.9
	Melting Point, °C	77.7	-
	% Crystallinity	17.2	-
25	1% Secant Modulus, kPa	29,662	24,346
	Tensile Strength, kPa	3,095	5,900
	Elongation, %	456	870
	<u>Productivity</u>		
	ppm Ti in Copolymer	4.6	5.9



It is noted that it would not be possible to copolymerize ethylene and butylene under the conditions employed in Example 8. The reason for this is that the dew point of the reaction mixture would exceed the temperature of the bed.

It is also noted that when the ratio of propylene to ethylene in Example 8 was increased to 1.9, reactor fouling occurred due to particle agglomeration forcing a halt to polymerization.

10

#### Example 9

Ethylene was copolymerized with propylene and ethylidene norbornene employing the same fluid bed reactor system employed in examples 3-4.

In this polymerization, silica-impregnated precursor composition prepared in accordance with Example 1(b) and partially activated in accordance with Example 2(c) was fed to the polymerization reactor along with a 5 percent solution of triethylaluminum in isopentane so as to provide a completely activated catalyst in the reactor having an aluminum:titanium molar ratio of 24:1.

Table 5 below summarizes the reaction conditions employed in the polymerization, and the properties of the polymer produced by such polymerization.

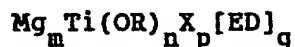
<u>Example</u>		<u>Table 5</u>	<u>9</u>
<u>Polymerization Conditions</u>			
	Temperature, °C		50
5	Pressure, kPa		2075
	Gas Velocity, ft./sec.		1.5
	Space-Time Yield (lbs./hr./ft <sup>3</sup> )		1.5
	Propylene/Ethylene Mol Ratio		0.91
10	Hydrogen/Ethylene Mol Ratio		0.23
	Mol % N <sub>2</sub> in Reaction Mixture		55.7
	Mol % H <sub>2</sub> in Reaction Mixture		4.7
	Mol % Ethylidene Norbornene in Reaction Mixture		4.3
15	<u>Polymer Properties</u>		
	Density, g/cm <sup>3</sup>		0.902
	Ethylidene Norbornene content, Mol %		2.3
	Melt Index, g/10 Min.		2.0
	Flow Index, g/10 Min.		74
20	Melt Flow Ratio		37
	Bulk Density, lbs/ft <sup>3</sup>		19.4
	Average Particle Size, in.		0.02
	1% Secant Modulus, kPa		93,772
	Tensile Strength, kPa		5,026
25	Elongation, %		948

CLAIMS

1. A continuous process for producing ethylene copolymers having a density of less than  $0.91 \text{ g/cm}^3$  and a 1% secant modulus of less than 140,000 kPa in a fluidized bed without particle agglomeration,

said copolymers containing no more than 94 mol percent of polymerized ethylene and at least 6 mol percent of polymerized alpha olefin containing from 3 to 8 carbon atoms,

which comprises continuously contacting, in a fluidized bed reaction zone, at a temperature of from  $10^\circ\text{C}$  up to  $80^\circ\text{C}$  and a pressure no greater than 7000 kPa, a gaseous mixture containing (a) ethylene and at least one higher alpha olefin containing from 3 to 8 carbon atoms, in a molar ratio of such higher alpha olefin to ethylene of from 0.35:1 to 8.0:1, and (b) at least 25 mol percent of at least one diluent gas, with particles of a catalyst system comprising a precursor composition having the formula



wherein R is an aliphatic or aromatic hydrocarbon radical containing from 1 to 14 carbon atoms, or  $\text{COR}'$  wherein R' is an aliphatic or aromatic hydrocarbon radical containing from 1 to 14 carbon atoms,

X is selected from the group consisting of Cl, Br, I, and mixtures thereof,

ED is an organic electron donor compound selected from the group consisting of alkyl esters of aliphatic and aromatic acids, aliphatic ethers, cyclic ethers and aliphatic ketones.

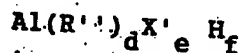
m is 0.5 to 56,

n is 0, 1 or 2,

p is 2 to 116, and

q is 2 to 85,

said precursor composition being diluted with an inert carrier material and completely activated with an organoaluminum compound having the formula



wherein  $\text{X}^{\text{I}}$  is Cl or OR<sup>II</sup>,

$\text{R}^{\text{I}}$  and  $\text{R}^{\text{II}}$  are saturated hydrocarbon radicals containing from 1 to 14 carbon atoms,

e is 0 to 1.5,

f is 0 or 1, and

$d + e + f = 3$ ,

said activator compound being employed in an amount such as to provide a total aluminum:titanium molar ratio in said reaction zone from 10:1 to 400:1.

2. A process as in claim 1 wherein said precursor composition is mechanically mixed with the inert carrier material and the blended mixture contains from 3 percent by weight to 50 percent by weight of the precursor composition.

3. A process as in claim 1 wherein the inert carrier material is impregnated with the precursor composition and the impregnated carrier material contains from 3 percent by weight to 50 percent by weight of the precursor composition.

4. A process as in any of claims 1 to 3 wherein the inert carrier material is silica.

5. A process as in any of claims 1 to 4 wherein the gaseous mixture contains hydrogen in an amount sufficient to produce a hydrogen to ethylene mol ratio of from 0.01:1 to 0.5:1.

6. A process as in any of claims 1 to 5 wherein the gaseous mixture contains from 33 mol percent to 95 mol percent of diluent gas, and the higher alpha olefin and ethylene are present in the mixture in a molar ratio of higher alpha olefin to ethylene of from 0.6:1 to 7.0:1.

7. A process as in any of claims 1 to 6 wherein the gaseous mixture contains from 0.1 mol percent to 10 mol percent of at least one diene.

8. A process as in claim 7 wherein the diene is ethylidene norbornene.

9. A process as in any one of claims 1 to 8 wherein X and X' are Cl, [ED] is tetrahydrofuran, n is 0, m is 1.5 to 5, p is 6 to 14, and q is 3 to 10.

10. A process as in any one of claims 1 to 9 wherein the precursor composition is composed of magnesium chloride, titanium trichloride, and tetrahydrofuran.

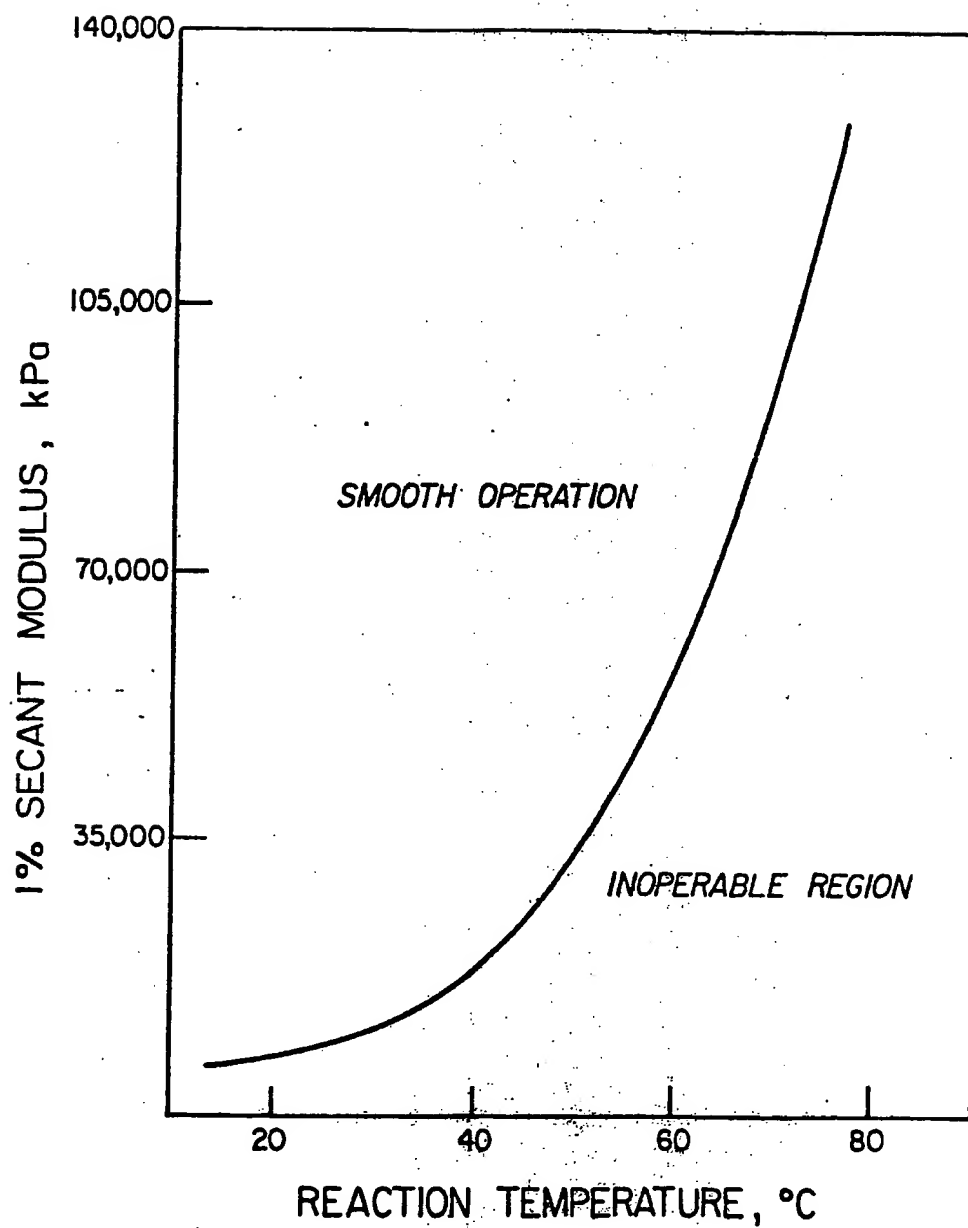
11. A process as in any one of claims 1 to 9 wherein the precursor composition is composed of

magnesium chloride, titanium tetrachloride, and tetrahydrofuran.

12. A process as in any one of claims 1 to 11 wherein the higher alpha olefin is propylene or butene-1.

13. A process as in any one of claims 1 to 12 wherein the gaseous mixture contains nitrogen.

14. Ethylene copolymers having a density of less than  $0.91 \text{ g/cm}^3$  and a 1% secant modulus of less than 140,000 kPa, obtainable by the process of any of claims 1-13.





European Patent  
Office

# EUROPEAN SEARCH REPORT

0120503

Application number

EP 84 10 3441

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. *)
X	GB-A-2 066 274 (NIPPON OIL) * Claims 1-11; page 4, lines 88-93; example 6 *  -----	1-14	C 08 F 2/16 C 08 F 2/34
			TECHNICAL FIELDS SEARCHED (Int. Cl. *)
			C 08 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 07-06-1984	Examiner WEBER H.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  & : member of the same patent family, corresponding document	